Ligand-Controlled, Complementary Stereoselectivity in the Platinum-Catalyzed Intramolecular Silaboration of Alkenes

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1. General

All reactions were performed in a drybox or using Schlenk technique under an atmosphere of nitrogen or argon with magnetic stirring. Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40–63 μm , 60 Å). ^1H NMR spectra were recorded on Varian GEMINI-2000 (300.07 MHz), Varian Mercury-400 (400.44 MHz), JEOL JNM-A500 (500.00 MHz), or JEOL JNM-ECA600 (600.17 MHz) spectrometers. ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (75.45 MHz), JEOL JNM-A400 (100.40 MHz), or JEOL JNM-A500 (125.65 MHz) spectrometers. ^{11}B NMR spectra were recorded on a Varian Mercury-400 (128.48 MHz) spectrometer. Chemical shifts were reported in ppm downfield from tetramethylsilane (for ^1H and ^{13}C) or $\text{BF}_3\cdot\text{OEt}_2$ (for ^{11}B). Infrared spectra were recorded on a SHIMADZU FTIR-8100 spectrometer. Elemental analyses were performed by Elemental Analysis Center of Kyoto University. High-resolution mass spectra were recorded on JEOL JMS-MS700 (CI) or JEOL JMS-HX110A (FAB) spectrometers.

2. Materials

Toluene, THF, and pentane were dried and degassed by The Ultimate Solvent System (GlassContour). $\text{Pt}(\text{dba})_2^1$ and $\text{Pd}(\text{dba})_2^2$ were prepared according to the literature method. All phosphines and phosphites were commercially available. Liquid phosphorus compounds were distilled before use. Iodobenzene, KF, 30% H_2O_2 aq. (WAKO), KHCO_3 , NaOAc , $\text{CsOH}\cdot\text{H}_2\text{O}$ (NACALAI TESQUE), $n\text{-BuLi}$ in hexane (MITSUWA) were used as received from the commercial sources. ClCH_2Br (NACALAI TESQUE) was distilled prior to use. Homoallylic alcohols were synthesized by the reaction of allylmagnesium chloride with aldehydes or diethylketone.

3. Preparation of borylsilanyl homoallyl ethers 1 and 3

3-1. Preparation of $\text{ClPh}_2\text{SiB}(\text{pin})$ (**15**, Scheme S1)

A silylborane **14** was prepared by the following procedure, according to our previous report.³ To a solution

Scheme S1.

of (isopropoxy)pinacolborane⁴ (**13**, 229 mmol) in hexane (100 mL) was added (diethylamino)diphenylsilyllithium (**12**),⁵ which was prepared from (diethylamino)diphenylsilyl chloride (**11**, 27.6 g, 95.3 mmol) and lithium (2.65 g, 381 mmol) in THF (90 mL), dropwise at 0 °C over 30 min. After the addition, cooling bath was removed. The mixture was stirred for 12 h at room temperature. The volatiles were removed *in vacuo* and then the residue was diluted with pentane. After removing the insoluble white solid by filtration under nitrogen atmosphere, the filtrate was concentrated. Recrystallization from pentane gave pure [(diethylamino)diphenylsilyl]pinacolborane (**14**, 34.5 g, 95%). **14**: ^{11}B NMR (128 MHz, C_6D_6) δ 33.6. ^1H NMR (400 MHz, CDCl_3) δ 7.60–7.62 (m, 4H), 7.33–7.35 (m, 6H), 2.94 (q, J = 6.8 Hz, 4H), 1.28 (s, 12H), 1.00 (t, J = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 137.8, 135.4, 128.8, 127.5, 83.4, 41.1, 25.0, 15.4.

To a CH_2Cl_2 (60 mL) solution of **14** (25.1 g, 65.7 mmol) was added a Et_2O solution of hydrochloric acid (1.0 M, 145 mL, 145 mmol) at 0 °C. The mixture was stirred at room temperature for 5 h. The white precipitate was removed by filtration under nitrogen atmosphere, resulting filtrate was concentrated. Bulb-to-bulb distillation under reducing pressure (190 °C/1.5 mmHg) gave (chlorodiphenylsilyl)pinacolborane (**15**) as white solid (21.4 g, 94%). **15**: ^{11}B NMR (128 MHz, C_6D_6) δ 32.3. ^1H NMR (300 MHz, CDCl_3) δ 7.69–7.73 (m, 4H), 7.36–7.47 (m, 6H), 1.32 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 134.6, 134.0, 130.3, 128.1, 84.7, 25.0. HRMS (CI) m/z calcd for $\text{C}_{18}\text{H}_{23}\text{BO}_2\text{ClSi}$ (MH^+): 345.1249, found: 345.1255.

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3-2. Reaction of homoallylic alcohols with ClPh₂SiB(pin) (Scheme S2)

Scheme S2

Typical procedure: To a CH₂Cl₂ solution of **15** (3.45 g, 10 mmol) and pyridine (0.97 mL, 12 mmol) was added a homoallylic alcohol (10 mmol) at 0 °C. A white salt was immediately precipitated. After stirring at 0 °C for 3 h, the volatiles were evaporated and the residue was diluted with pentane. The salt was filtrated off through celite pad under nitrogen atmosphere. The filtrate was concentrated to give a borylsilanyl homoallylic ether, which was usually used for the Pt-catalyzed intramolecular silaboration without further purification. The compound may be purified by silica-gel column chromatography in drybox, if necessary.

4-Ethyl-4-[diphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyloxy]-1-hexene (1). ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.69 (m, 4H), 7.27-7.36 (m, 6H), 5.85 (ddt, *J* = 16.8, 10.4, 7.2 Hz, 1H), 4.97-5.03 (m, 2H), 2.36 (dt, *J* = 7.2, 1.2 Hz, 2H), 1.59 (dq, *J* = 7.2, 1.2 Hz, 4H), 1.30 (s, 12H), 0.84 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 139.0, 135.3, 134.6, 129.0, 127.5, 116.7, 83.7, 79.4, 43.4, 31.5, 25.0, 8.3. HRMS (CI) *m/z* calcd for C₂₆H₃₈BO₃Si (MH⁺): 437.2683, found: 437.2684.

4-[Diphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyloxy]-5-methyl-1-hexene (3a). ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.68 (m, 4H), 7.31-7.39 (m, 6H), 5.81 (ddt, *J* = 17.0, 10.2, 7.2 Hz, 1H), 4.93-5.02 (m, 2H), 3.77 (dt, *J* = 6.0, 4.8 Hz, 1H), 2.21-2.34 (m, 2H), 1.79 (d-septet, *J* = 6.8, 4.8 Hz, 1H), 1.30 (s, 12H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 137.3, 135.9, 134.8, 129.3, 127.6, 116.2, 83.7, 78.5, 38.5, 32.5, 25.1, 18.7, 17.3. HRMS (CI) *m/z* calcd for C₂₅H₃₆BO₃Si (MH⁺): 423.2527, found: 423.2514.

4-[Diphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyloxy]-1-petene (3b). ¹H NMR (400 MHz, CDCl₃) δ

7.65-7.69 (m, 4H), 7.32-7.40 (m, 6H), 5.82 (ddt, *J* = 17.2, 10.4, 7.2 Hz, 1H), 4.98-5.06 (m, 2H), 4.07 (sextet, *J* = 6.0 Hz, 1H), 2.39 (dddt, *J* = 13.6, 7.2, 5.6, 1.2 Hz, 1H), 2.24 (ddt, *J* = 13.6, 7.2, 1.2 Hz, 1H), 1.31 (s, 12H), 1.20 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 136.8, 135.4, 134.7, 134.6, 129.4 (2C), 127.6 (2C), 116.5, 83.7, 70.0, 44.0, 25.0, 22.9. HRMS (CI) *m/z* calcd for C₂₃H₃₁BO₃Si (MH⁺): 395.2214, found: 395.2213.

4-[Diphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyloxy]-6-methyl-1-heptene (3c). ¹H NMR (400 MHz, CDCl₃) δ 7.63-7.68 (m, 4H), 7.31-7.39 (m, 6H), 5.76-5.86 (m, 1H), 4.96-5.01 (m, 2H), 4.00 (ddt, *J* = 8.0, 5.6, 5.2 Hz, 1H), 2.24-2.35 (m, 2H), 1.68-1.78 (m, 1H), 1.49 (ddd, *J* = 13.6, 8.0, 5.4 Hz, 1H), 1.30 (s, 12H), 1.24-1.31 (m, 1H), 0.82 (d, *J* = 6.4 Hz, 3H), 0.76 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 137.1, 135.4, 134.8, 129.4, 127.6, 116.6, 83.7, 72.1, 45.9, 42.2, 25.1, 24.4, 23.3, 22.4. HRMS (CI) *m/z* calcd for C₂₆H₃₈BO₃Si (MH⁺): 437.2683, found: 437.2679.

4-[Diphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyloxy]-6-phenyl-1-hexene (3d). ¹¹B NMR (128 MHz, CDCl₃) δ 33.0. ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.60 (m, 4H), 7.22-7.30 (m, 6H), 7.10-7.16 (m, 2H), 7.02-7.05 (m, 1H), 6.98-7.00 (m, 2H), 5.70 (ddt, *J* = 17.2, 10.4, 6.8 Hz, 1H), 4.87-4.93 (m, 2H), 3.91 (quintet, *J* = 6.0 Hz, 1H), 2.58-2.66 (m, 1H), 2.43-2.50 (m, 1H), 2.19-2.32 (m, 2H), 1.68-1.77 (m, 2H), 1.18 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 142.7, 136.99, 136.95, 135.1, 134.8 (2C), 129.5 (2C), 128.3, 128.2, 127.71, 127.68, 125.5, 116.8, 83.8, 73.5, 41.7, 38.2, 31.7, 25.1. HRMS (CI) *m/z* calcd for C₃₀H₃₈BO₃Si (MH⁺): 485.2683, found: 485.2682.

4-[Diphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyloxy]-4-phenyl-1-butene (3e). ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.68 (m, 2H), 7.55-7.59 (m, 2H), 7.18-7.41 (m, 11H), 5.73 (ddt, *J* = 17.0, 10.2, 7.0 Hz, 1H), 4.94-5.00 (m, 2H), 4.92 (t, *J* = 6.4 Hz, 1H), 2.61-2.68 (m, 1H), 2.48-2.55 (m, 1H), 1.22 (s, 6H), 1.21 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 144.1, 136.7, 136.4, 134.9, 134.8, 134.7, 129.48, 129.35, 127.8, 127.65, 127.55, 126.9, 126.4, 116.9, 83.7, 76.0, 44.8, 25.00, 24.96. HRMS (CI) *m/z* calcd for C₂₈H₃₄BO₃Si (MH⁺): 457.2370, found: 457.2372.

5,5-Dimethyl-4-[(diphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyloxy)-1-hexene] (3f). ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.68 (m, 4H), 7.27-7.37 (m, 6H), 5.77 (ddt, J = 16.8, 10.0, 7.2 Hz, 1H), 4.78-4.92 (m, 2H), 3.65 (dd, J = 7.6, 3.6 Hz, 1H), 2.29-2.36 (m, 1H), 2.19-2.27 (m, 1H), 1.29 (s, 12H), 0.89 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 137.6, 134.9, 129.2, 127.49, 127.46, 115.8, 83.6, 82.5, 37.7, 36.1, 26.5, 25.1. HRMS (CI) m/z calcd for $\text{C}_{26}\text{H}_{38}\text{BO}_3\text{Si}$ (MH^+): 437.2684, found: 437.2675.

4. Pt-catalyzed intramolecular silaboration of 1 (eq 1)

A toluene (0.2 mL) solution of $\text{Pt}(\text{dba})_2$ (10 mg, 0.015 mmol), PPh_3 (7.9 mg, 0.033 mmol), and **1** (131 mg, 0.30 mmol) was heated at 110 °C for 5 h. After evaporation of the volatile materials, the residue was purified by column chromatography (Hexane: Et_2O = 20:1) to give **2** in 87% yield (109 mg).

5,5-Dimethyl-2,2-diphenyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (2). ^1H NMR (400 MHz, CDCl_3) δ 7.75-7.78 (m, 2H), 7.60-7.64 (m, 2H), 7.33-7.43 (m, 6H), 2.24 (dd, J = 12.8, 8.0 Hz, 1H), 1.92-2.02 (m, 1H), 1.49-1.87 (m, 5H), 1.15 (s, 6H), 1.13 (s, 6H), 1.00 (t, J = 7.6 Hz, 3H), 0.89-0.93 (m, 2H), 0.87 (t, J = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 135.6, 135.3, 135.0, 133.6, 129.6 (2C), 127.43, 127.40, 84.1, 83.0, 44.5, 32.5, 30.8, 24.9, 24.5, 18.4, 12.2 (br, C-B), 8.69, 8.65. HRMS (CI) m/z calcd for $\text{C}_{26}\text{H}_{37}\text{BO}_3\text{Si}$ (MH^+): 435.2527, found: 435.2523.

5. Screening of the ligand for the Pt-catalyzed intramolecular silaboration of 3a (Table 1)

A toluene (0.3 mL) solution of $\text{Pt}(\text{dba})_2$ (7.9 mg, 0.012 mmol), phosphorus ligand (0.026 mmol), and **3a** (100 mg, 0.24 mmol) was heated at 110 °C. The reaction was monitored by GC. The substrate was consumed within 24 h. The *trans/cis* ratio of the product **4a** was determined by ^1H NMR analysis along with HPLC analysis [column: Cica-MERCK LiChrosorb CN (4 mm x 250 mm); eluent: hexane/1,2-dichloroethane = 96:4; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 19.2 (*cis*), 28.5 (*trans*) min]. The yield of **4a** was also determined by ^1H NMR analysis using dibenzyl ether as internal standard. Isolation of **4a** was performed by bulb-to-bulb distillation.

(3R*,5S*)-2,2-Diphenyl-5-(1-methylethyl)-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-

silacyclopentane (trans-4a). ^1H NMR (400 MHz, CDCl_3) δ 7.70-7.73 (m, 2H), 7.55-7.58 (m, 2H), 7.30-7.44 (m, 6H), 4.01 (dt, J = 6.8, 5.0 Hz, 1H), 2.04 (dt, J = 12.8, 6.8 Hz, 1H), 1.67-1.87 (m, 3H), 1.13 (s, 6H), 1.09 (s, 6H), 1.00 (d, J = 6.4 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.82-0.95 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 135.5, 135.3, 134.7, 133.7, 129.8, 129.7, 127.62, 127.58, 83.0, 82.7, 38.1, 34.2, 25.0, 24.5, 19.2, 18.6, 18.1. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for $\text{C}_{25}\text{H}_{35}\text{BO}_3\text{Si}$: C, 71.08; H, 8.35. Found: C, 71.06; H, 8.49 (A *trans/cis* mixture was used for elemental analysis).

(3S*,5S*)-2,2-Diphenyl-5-(1-methylethyl)-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (cis-4a). ^1H NMR (400 MHz, CDCl_3) δ 7.72-7.75 (m, 2H), 7.60-7.63 (m, 2H), 7.32-7.42 (m, 6H), 3.72 (ddd, J = 10.8, 6.8, 4.0 Hz, 1H), 2.28 (ddd, J = 12.8, 7.6, 4.0 Hz, 1H), 1.77-1.89 (m, 2H), 1.35 (dt, J = 12.8, 10.8 Hz, 1H), 1.13 (s, 6H), 1.11 (s, 6H), 1.08 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H), 0.84-0.97 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.4, 135.3, 135.2, 133.4, 129.8, 129.7, 127.6, 127.5, 83.06, 83.05, 39.7, 34.9, 24.9, 24.5, 20.5, 19.4, 18.3. Elemental analysis was carried out for a *trans/cis* mixture. See characterization data of *trans-4a*.

6. Pt-catalyzed intramolecular silaboration of 3 (Table 2)

Typical procedure: A toluene (0.6 mL) solution of $\text{Pt}(\text{dba})_2$ (7.9 mg, 0.012 mmol), PCyPh_2 (7.0 mg, 0.026 mmol) or **5** (17 mg, 0.026 mmol), and **3** (0.24 mmol) was heated at 110 °C. The reaction was monitored by GC. After consumption of the substrate, volatile materials were removed *in vacuo*. The *trans/cis* ratio of the product **4** was determined by ^1H NMR analysis. The crude **4** was purified by bulb-to-bulb distillation under reducing pressure. In the reactions of **3c-e** using Pt/PCyPh_2 catalyst, small amounts of structure-undefined side products were formed along with **4c-e**, which could not separate by distillation. In such cases, purification was carried out using HPLC [column: Cica-MERCK LiChrosorb Si 60 (10 mm x 250 mm); eluent: hexane: Et_2O = 50:1-30:1]. For **4c** and **4f**, the *trans/cis* ratio was also checked by HPLC analysis [column: Cica-MERCK LiChrosorb CN (4 mm x 250 mm); eluent: hexane/1,2-dichloroethane = 96:4; flow rate: 0.6 mL/min; detection wavelength: 220 nm; **4c**: T_R = 19.2 (*cis*), 28.2 (*trans*) min; **4f**: T_R = 12.2 (*cis*), 14.7 (*trans*) min]. For **4d** and **4e**, the *trans/cis* ratio was also checked by GC analysis [column: J&W Scientific DB-1 (0.25 mm ID x 15 m); carrier gas: N_2 ; detection: FID; oven temp: 80 °C (hold 1 min) to 290 °C (30 °C/min); **4d**: T_R = 14.9 (*trans*), 15.2 (*cis*) min; **4e**: T_R = 12.9 (*trans*), 13.3 (*cis*) min].

(3*R,5*R**)-2,2-Diphenyl-5-methyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*trans-4b*).** According to the typical procedure, **3b** (100 mg, 0.25 mmol) was reacted in the presence of Pt/PCyPh₂ catalyst. The *trans/cis* ratio of the product was determined as 81:19 by ¹H NMR analysis of the crude mixture. Bulb-to-bulb distillation afforded a mixture of **4b** and a structure-undefined side product [LRMS (CI) *m/z* 393 (MH⁺)] with the ratio of 4:1 (GC). Because *trans-4b* was unstable for chromatography, the yield of **4b** was determined as 71% according to the ratio. After oxidation of the mixture under Tamao conditions, (2*S**,4*R**)-1,2,4-pentanetriol was isolated by column chromatography (AcOEt:MeOH = 20:1) in 43% yield from **3b**, indicating the reasonableness of the yield of **4b** along with confirming of the structure of **4b**. *trans-4b*: ¹H NMR (600 MHz, C₆D₆) δ 7.88-7.90 (m, 2H), 7.78-7.80 (m, 2H), 7.10-7.22 (m, 6H), 4.48 (sextet, *J* = 6.0 Hz, 1H), 2.06 (dq, *J* = 10.2, 7.2 Hz, 1H), 1.84 (dd, *J* = 7.2, 6.0 Hz, 2H), 1.26 (d, *J* = 6.0 Hz, 3H), 0.97 (s, 6H), 0.94 (s, 6H), 0.84-0.90 (m, 2H). (2*S**,4*R**)-1,2,4-pentanetriol⁶: ¹H NMR (400 MHz, D₂O) δ 3.98-4.06 (m, 1H), 3.84-3.89 (m, 1H), 3.57-3.63 (m, 1H), 3.45-3.52 (m, 1H), 1.54-1.58 (m, 2H), 1.23 (d, *J* = 6.0 Hz, 3H).

(3*S,5*R**)-2,2-Diphenyl-5-methyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*cis-4b*).** According to the typical procedure, **3b** (101 mg, 0.25 mmol) was reacted in the presence of Pt/5 catalyst. The product **4b** was isolated in 93% yield (*trans/cis* = 7:93). *cis-4b*: ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.76 (m, 2H), 7.61-7.63 (m, 2H), 7.33-7.44 (m, 6H), 4.19 (ddq, *J* = 11.2, 6.0, 4.0 Hz, 1H), 2.33 (ddd, *J* = 12.8, 7.6, 4.0 Hz, 1H), 1.88 (ddt, *J* = 12.8, 8.8, 7.6 Hz, 1H), 1.43 (d, *J* = 6.0 Hz, 3H), 1.33 (dt, *J* = 12.8, 11.2 Hz, 1H), 1.14 (s, 6H), 1.12 (s, 6H), 0.82-0.98 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 135.3, 135.1, 134.9, 133.1, 129.9, 129.8, 127.6, 127.5, 83.1, 74.1, 44.5, 24.9, 24.5, 23.4, 20.7. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (CI) *m/z* calcd for C₂₃H₃₂BO₃Si (MH⁺): 395.2214, found: 395.2213.

(3*R,5*R**)-2,2-Diphenyl-5-(2-methylpropyl)-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*trans-4c*).** According to the

typical procedure, **3c** (100 mg, 0.23 mmol) was reacted in the presence of Pt/PCyPh₂ catalyst. The product **4c** was isolated in 79% yield (*trans/cis* = 82:18). *trans-4c*: ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.75 (m, 2H), 7.58-7.61 (m, 2H), 7.32-7.44 (m, 6H), 4.41-4.47 (m, 1H), 1.81-1.98 (m, 4H), 1.60 (ddd, *J* = 13.6, 8.4, 6.0 Hz, 1H), 1.29 (ddd, *J* = 13.6, 8.0, 4.8 Hz, 1H), 1.14 (s, 6H), 1.11 (s, 6H), 0.97 (d, *J* = 6.4 Hz, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.85-0.93 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 135.6, 135.2, 134.7, 133.5, 129.72, 129.68, 127.6 (2C), 82.0, 75.5, 46.9, 41.4, 25.1, 25.0, 24.5, 23.2, 22.5, 17.9, 12.2 (br, C-B). HRMS (CI) *m/z* calcd for C₂₆H₃₈BO₃Si (MH⁺): 437.2684, found: 437.2686.

(3*S,5*R**)-2,2-Diphenyl-5-(2-methylpropyl)-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*cis-4c*).** According to the typical procedure, **3c** (102 mg, 0.23 mmol) was reacted in the presence of Pt/5 catalyst. The product **4c** was isolated in 83% yield (*trans/cis* = 6:94). *cis-4c*: ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.76 (m, 2H), 7.59-7.62 (m, 2H), 7.33-7.43 (m, 6H), 4.10 (dddd, *J* = 10.8, 7.6, 5.6, 4.0 Hz, 1H), 2.32 (ddd, *J* = 12.8, 7.6, 4.0 Hz, 1H), 1.78-1.93 (m, 2H), 1.68-1.75 (m, 1H), 1.45 (ddd, *J* = 13.2, 7.6, 5.6 Hz, 1H), 1.30 (dt, *J* = 12.8, 10.8 Hz, 1H), 1.14 (s, 6H), 1.11 (s, 6H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.82-0.92 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 135.3, 135.1 (2C), 133.3, 129.8, 129.7, 127.6, 127.5, 83.1, 76.2, 47.4, 43.1, 25.3, 25.0, 24.5, 23.2, 22.9, 20.4, 11.9 (br, C-B). HRMS (CI) *m/z* calcd for C₂₆H₃₈BO₃Si (MH⁺): 437.2683, found: 437.2683.

(3*R,5*R**)-2,2-Diphenyl-5-(2-phenylethyl)-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*trans-4d*).** According to the typical procedure, **3d** (100 mg, 0.21 mmol) was reacted in the presence of Pt/PCyPh₂ catalyst. The product **4d** was isolated in 76% yield (*trans/cis* = 84:16). *trans-4d*: ¹H NMR (400 MHz, CDCl₃) δ 7.74-7.78 (m, 2H), 7.57-7.61 (m, 2H), 7.32-7.46 (m, 6H), 7.24-7.29 (m, 2H), 7.15-7.19 (m, 3H), 4.35-4.41 (m, 1H), 2.85 (ddd, *J* = 13.6, 10.0, 5.2 Hz, 1H), 2.72 (ddd, *J* = 13.6, 10.0, 6.4 Hz, 1H), 1.76-2.06 (m, 5H), 1.13 (s, 6H), 1.10 (s, 6H), 0.83-0.94 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 142.5, 135.4, 135.3, 134.7, 133.3, 129.83, 129.78, 128.5, 128.2, 127.7, 127.6, 125.6, 83.0, 76.7, 41.0, 39.7, 32.6, 25.0, 24.5, 18.0, 12.0 (br, C-B). HRMS (CI) *m/z* calcd for C₃₀H₃₈BO₃Si (MH⁺): 485.2683, found: 485.2664.

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(3*S,5*R**)-2,2-Diphenyl-5-(2-phenylethyl)-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*cis-4d*).** According to the typical procedure, **3d** (101 mg, 0.21 mmol) was reacted in the presence of Pt/**5** catalyst. The product **4d** was isolated in 82% yield (*trans/cis* = 8:92). *cis-4d*: ¹H NMR (400 MHz, CDCl₃) δ 7.75-7.78 (m, 2H), 7.63-7.67 (m, 2H), 7.35-7.45 (m, 6H), 7.25-7.32 (m, 4H), 7.18-7.21 (m, 1H), 4.03-4.10 (m, 1H), 2.91 (ddd, *J* = 13.6, 10.0, 5.6 Hz, 1H), 2.80 (ddd, *J* = 13.6, 10.0, 6.4 Hz, 1H), 2.36 (ddd, *J* = 12.8, 7.6, 4.0 Hz, 1H), 2.06-2.15 (m, 1H), 1.93-2.01 (m, 1H), 1.81-1.90 (m, 1H), 1.40 (dt, *J* = 12.8, 10.8 Hz, 1H), 1.15 (s, 6H), 1.12 (s, 6H), 0.86-0.99 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 142.4, 135.3, 135.1 (2C), 133.2, 129.9, 129.8, 128.5, 128.3, 127.6, 125.6, 83.1, 77.1, 42.5, 39.7, 32.4, 24.9, 24.5, 20.5, 11.9 (br, C-B). HRMS (CI) *m/z* calcd for C₃₀H₃₈BO₃Si (MH⁺): 485.2683, found: 485.2685.

(3*R,5*S**)-2,2-Diphenyl-5-phenyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*trans-4e*).** According to the typical procedure, **3e** (100 mg, 0.22 mmol) was reacted in the presence of Pt/PCyPh₂ catalyst. The product **4e** was isolated in 80% yield (*trans/cis* = 88:12). *trans-4e*: ¹H NMR (400 MHz, CDCl₃) δ 7.74-7.78 (m, 2H), 7.63-7.66 (m, 2H), 7.34-7.48 (m, 8H), 7.28-7.32 (m, 2H), 7.21-7.24 (m, 1H), 5.43 (t, *J* = 6.6 Hz, 1H), 2.20-2.23 (m, 2H), 1.91-1.99 (m, 1H), 1.13 (s, 6H), 1.08 (s, 6H), 0.90-1.04 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 135.4, 134.9, 134.8, 133.1, 130.01, 129.99, 128.2, 127.8, 127.7, 126.9, 125.5, 83.1, 78.6, 44.2, 25.0, 24.5, 18.1, 11.9 (br, C-B). HRMS (CI) *m/z* calcd for C₂₈H₃₄BO₃Si (MH⁺): 457.2370, found: 457.2363.

(3*S,5*S**)-2,2-Diphenyl-5-phenyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*cis-4e*).** According to the typical procedure, **3e** (101 mg, 0.22 mmol) was reacted in the presence of Pt/**5** catalyst. The product **4e** was isolated in 83% yield (*trans/cis* = 7:93). *cis-4e*: ¹¹B NMR (128 MHz, CDCl₃) δ 33.1. ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.83 (m, 2H), 7.69-7.71 (m, 2H), 7.50-7.52 (m, 2H), 7.36-7.46 (m, 8H), 7.26-7.29 (m, 1H), 5.07 (dd, *J* = 11.2, 4.0 Hz, 1H), 2.63 (ddd, *J* = 12.8, 7.2, 4.0 Hz, 1H), 1.98-2.08 (m, 1H), 1.66 (dt, *J* = 12.8, 11.2 Hz, 1H), 1.15 (s, 6H), 1.13 (s, 6H), 0.90-1.03 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 144.1, 135.4, 135.1, 134.8, 133.0, 130.0 (2C), 128.3, 127.7, 127.6, 127.1, 125.5, 83.2, 79.1, 45.6, 25.0, 24.6, 21.2. The boron-

bound carbon was not detected due to quadrupolar relaxation. HRMS (CI) *m/z* calcd for C₂₈H₃₄BO₃Si (MH⁺): 457.2370, found: 457.2357.

(3*R,5*S**)-5-(1,1-Dimethylethyl)-2,2-diphenyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*trans-4f*).** According to the typical procedure, **3f** (100 mg, 0.23 mmol) was reacted in the presence of Pt/PCyPh₂ catalyst. The product **4f** was isolated in 96% yield (*trans/cis* = 92:8). *trans-4f*: ¹H NMR (400 MHz, CDCl₃) δ 7.70-7.73 (m, 2H), 7.53-7.55 (m, 2H), 7.29-7.44 (m, 6H), 3.99 (dd, *J* = 9.6, 4.8 Hz, 1H), 2.03 (ddd, *J* = 13.2, 9.6, 8.0 Hz, 1H), 1.85 (dq, *J* = 8.0, 3.6 Hz, 1H), 1.72 (ddd, *J* = 13.2, 4.8, 3.6 Hz, 1H), 1.14 (s, 6H), 1.09 (s, 6H), 0.93 (s, 9H), 0.81-1.00 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 135.4, 135.2, 134.6, 134.0, 129.7, 129.6, 127.6, 127.5, 84.9, 83.0, 35.9, 34.8, 26.0, 25.0, 24.5, 12.8 (br, C-B). HRMS (CI) *m/z* calcd for C₂₆H₃₈BO₃Si (MH⁺): 437.2683, found: 437.2685.

(3*S,5*S**)-5-(1,1-Dimethylethyl)-2,2-Diphenyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-oxa-2-silacyclopentane (*cis-4f*).** According to the typical procedure, **3f** (97 mg, 0.22 mmol) was reacted in the presence of Pt/**5** catalyst. The product **4f** was isolated by column chromatography (pentane:THF = 40:1) in 85% yield (*trans/cis* = 6:94). *cis-4f*: ¹¹B NMR (128 MHz, CDCl₃) δ 34.0. ¹H NMR (400 MHz, CDCl₃) δ 7.75-7.78 (m, 2H), 7.60-7.63 (m, 2H), 7.31-7.44 (m, 6H), 3.67 (dd, *J* = 11.6, 3.6 Hz, 1H), 2.19 (ddd, *J* = 12.4, 7.6, 3.6 Hz, 1H), 1.74-1.84 (m, 1H), 1.42 (q, *J* = 12.4 Hz, 1H), 1.15 (s, 6H), 1.12 (s, 6H), 1.01 (s, 9H), 0.85-1.00 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 135.7, 135.3, 135.0, 133.5, 129.61, 129.57, 127.4 (2C), 85.3, 82.9, 37.3, 34.6, 26.0, 24.9, 24.4, 20.9, 12.3 (br, C-B). HRMS (CI) *m/z* calcd for C₂₆H₃₈BO₃Si (MH⁺): 437.2683, found: 437.2678.

7. Assignment of stereochemistry of **4** (Scheme S3)

To a mixture of **4f** (107 mg, 0.25 mmol), KF (117 mg, 2.0 mmol), and KHCO₃ (95 mg, 0.98 mmol) in THF/MeOH (0.25 mL/0.25 mL) was slowly added 30% H₂O₂ aq. (0.37 mL) at 0 °C. The mixture was stirred overnight at room temperature. After addition of aqueous Na₂S₂O₃ solution, the mixture was extracted with EtOAc and the organic layer was dried over anhydrous MgSO₄. The triol **16** was isolated by column chromatography (EtOAc) in 72-69% yield.

To a solution of **16** (22 mg, 0.14 mmol) in pyridine (0.4 mL) was added pivaloyl chloride (25 mg, 0.20 mmol) at room temperature and stirred for 10 h. After removing of the volatile materials *in vacuo*, water was added and the

Scheme S3.

resulting mixture was extracted with Et₂O. The extract was dried over anhydrous MgSO₄ and concentrated to give 5,5-dimethyl-1-pivaloyloxy-2,4-hexandiol. The diol was dissolved in acetone (0.5 mL) and the solution was treated with 2,2-dimethoxypropane (0.058 mL, 0.48 mmol) and *p*-toluenesulfonic acid (0.26 mg, 0.0014 mmol). The mixture was stirred for 10 h at room temperature. Aqueous NaHCO₃ solution was added and the resulting mixture was extracted with Et₂O. After drying over anhydrous MgSO₄, **17** was isolated by column chromatography (hexane:Et₂O = 20:1). According to the literature,⁷ the stereochemistry of **17** was assigned by ¹³C NMR chemical shifts of the isopropylideneacetal moiety. Thus the isomer having 23.9, 24.6, and 100.4 ppm was assigned as *trans*, whereas that having 19.6, 30.0, and 98.4 ppm was assigned as *cis*.

(4*R,6*S**)-6-*tert*-Butyl-2,2-dimethyl-4-pivaloxymethyl-1,3-dioxane (*trans*-17).** ¹H NMR (500 MHz, CDCl₃) δ 4.14 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.98 (dd, *J* = 11.0, 7.0 Hz, 1H), 3.92-3.95 (m, 1H), 3.43 (dd, *J* = 10.0, 6.5 Hz, 1H), 1.68 (ddd, *J* = 12.5, 10.0, 6.0 Hz, 1H), 1.42 (ddd, *J* = 12.5, 10.0, 6.5 Hz, 1H), 1.32 (s, 3H), 1.31 (s, 3H), 1.20 (s, 9H), 0.86 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 178.4, 100.4, 73.4, 66.1, 65.6, 38.8, 33.3, 29.5, 27.1, 25.2, 24.6, 23.9. HRMS (FAB) *m/z* calcd for C₁₆H₃₁O₄ (MH⁺): 287.2222, found: 287.2218.

(4*S,6*S**)-6-*tert*-Butyl-2,2-dimethyl-4-pivaloxymethyl-1,3-dioxane (*cis*-17).** ¹H NMR (400 MHz, CDCl₃) δ 4.00-4.11 (m, 3H), 3.44 (dd, *J* = 11.6, 2.4 Hz, 1H), 1.37-1.42 (m, 1H), 1.40 (s, 3H), 1.37 (s, 3H), 1.20-1.29 (m, 1H), 1.22 (s, 9H), 0.87 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 178.3, 98.4, 75.8, 67.7, 67.0, 38.9, 33.6, 30.0, 27.5, 27.2, 25.4,

19.6. HRMS (CI) *m/z* calcd for C₁₆H₃₁O₄ (MH⁺): 287.2222, found: 287.2219.

8. Terminal C–B bond selective oxidation of **2** (eq 2)

To a mixture of **2** (81 mg, 0.19 mmol) and 5.0 M aqueous solution of NaOAc (0.28 mL, 1.4 mmol) in THF (0.2 mL) was added 30% aqueous solution of H₂O₂ (0.11 mL) slowly at 0 °C. The mixture was stirred overnight at room temperature. After addition of aqueous solution of Na₂S₂O₃, the mixture was extracted with Et₂O and the organic layer was dried over anhydrous MgSO₄. The alcohol **6** was isolated by column chromatography (hexane:Et₂O = 2:1) in 87% yield (53 mg).

5,5-Diethyl-3-hydroxymethyl-1-oxa-2-silacyclopentane (6**):** IR (neat): 3380 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.70-7.72 (m, 2H), 7.57-7.59 (m, 2H), 7.33-7.46 (m, 6H), 3.74 (dd, *J* = 10.5, 7.5 Hz, 1H), 3.68 (dd, *J* = 10.5, 9.0 Hz, 1H), 2.25 (dd, *J* = 12.5, 8.0 Hz, 1H), 2.12-2.19 (m, 1H), 1.85 (dq, *J* = 14.0, 7.5 Hz, 1H), 1.74 (dq, *J* = 14.0, 7.5 Hz, 1H), 1.57-1.64 (m, 2H), 1.48-1.55 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 135.1, 134.9, 134.4, 133.6, 130.1, 130.0, 127.9, 127.8, 85.1, 64.4, 38.5, 32.6, 31.0, 28.8, 8.7, 8.5. Anal. Calcd for C₂₀H₂₆O₂Si: C, 73.57; H, 8.03. Found: C, 73.45; H, 7.96.

9. Suzuki-Miyaura cross-coupling of *cis*-4a with iodobenzene (eq 3)

The conditions reported by Hartwig⁸ were applied to this cross-coupling with a little modification. A mixture of *cis*-**4a** (*trans/cis* = 7:93, 80 mg, 0.19 mmol), iodobenzene (116 mg, 0.57 mmol), Pd(dba)₂ (11 mg, 0.019 mmol), DIPPF (7.9 mg, 0.019 mmol), and CsOH·H₂O (64 mg, 0.38 mmol) in 1,4-dioxane/H₂O (0.4 mL/0.2 mL) was heated at 80 °C for 24 h. After cooling of the mixture to room temperature, the volatile materials were removed *in vacuo*. Water was added to the residue and then the resulting mixture was extracted with Et₂O. The extracts were dried over anhydrous Na₂SO₄. Purification of the mixture by column chromatography (hexane:Et₂O = 40:1) afforded *cis*-**7** in 56% yield (40 mg, *trans/cis* = 7:93).

(3*S,5*S**)-2,2-diphenyl-5-(1-methylethyl)-3-phenylmethyl-1-oxa-2-silacyclopentane (*cis*-7):** ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.56 (m, 2H), 7.44-7.48 (m, 1H), 7.30-7.42 (m, 7H), 7.16-7.25 (m, 3H), 6.99-7.01 (m, 2H), 3.74 (ddd, *J* = 11.2, 6.8, 3.6 Hz, 1H), 2.81 (dd, *J* = 13.6, 8.0

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Hz, 1H), 2.66 (dd, $J = 13.6, 8.8$ Hz, 1H), 2.22 (ddd, $J = 12.8, 7.2, 3.6$ Hz, 1H), 1.94-2.03 (m, 1H), 1.90 (octet, $J = 6.8$ Hz, 1H), 1.52 (dt, $J = 12.8, 11.2$ Hz, 1H), 1.09 (d, $J = 6.8$ Hz, 3H), 0.99 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 142.5, 135.3, 134.7, 134.5, 133.6, 130.1, 129.9, 128.6, 128.2, 127.8, 127.7, 125.8, 83.2, 37.1, 36.6, 34.8, 29.1, 19.3, 18.3. Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{OSi}$: C, 80.59; H, 7.57. Found: C, 80.82; H, 7.60.

10. Complementary synthesis of a pair of diastereomers of 1,3,5-triol **9** (Scheme 1)

10-1. Homologation of **4a**

A THF (0.26 mL) solution of ClCH_2Br (34 mg, 0.26 mmol) and **4a** (100 mg, 0.24 mmol) was cooled to -95°C in acetone/liquid nitrogen bath. $n\text{-BuLi}$ (1.6 M solution of hexane, 0.26 mmol) was added slowly to the mixture with stirring. The resulting solution was stirred at -95°C for 30 min and then gradually warmed to room temperature. After stirring for 8 h, aqueous NH_4Cl was added to the solution and the resulting was extracted with Et_2O . The collected organic layer was dried over anhydrous MgSO_4 . The product **8** was isolated by bulb-to-bulb distillation.

(3R*,5S*)-2,2-Diphenyl-5-(1-methylethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-1-oxa-2-silacyclopentane (*trans*-8**)**. Homologation of *trans*-**3a** (*trans/cis* = 87:13, 100 mg, 0.24 mmol) was carried out according to the procedure described above. Bulb-to-bulb distillation of the crude mixture afforded *trans*-**8** in 81% yield (*trans/cis* = 87:13) with double homologated product (3%), unreacted starting compound (3%), and small amount of structure-undefined impurities. *trans*-**8**: ^1H NMR (400 MHz, CDCl_3) δ 7.66-7.68 (m, 2H), 7.54-7.56 (m, 2H), 7.31-7.44 (m, 6H), 4.02 (dt, $J = 7.2, 6.0$ Hz, 1H), 2.06 (ddd, $J = 13.2, 7.6, 6.0$ Hz, 1H), 1.84-1.90 (m, 1H), 1.53-1.73 (m, 3H), 1.41-1.50 (m, 1H), 1.20 (s, 12H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.89 (d, $J = 6.8$ Hz, 3H), 0.80-0.87 (m, 1H), 0.68-0.76 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 135.4, 135.0, 134.5, 133.8, 129.8 (2C), 127.8, 127.6, 83.2, 82.9, 34.9, 34.3, 26.3, 24.82, 24.77, 24.5, 19.3, 18.8. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (CI) m/z calcd for $\text{C}_{26}\text{H}_{36}\text{BO}_3\text{Si}$ (MH^+): 435.2527, found: 435.2522

(3S*,5S*)-2,2-Diphenyl-5-(1-methylethyl)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-1-oxa-2-silacyclopentane (*cis*-8**)**. Homologation of *cis*-**3a** (*trans/cis* = 7:93, 100 mg, 0.24 mmol) was carried out according to the procedure described above. Bulb-to-bulb distillation of the crude mixture afforded *cis*-**8** in 84% yield (*trans/cis* = 7:93) with double homologated product (6%)

and unreacted starting compound (2%). *cis*-**8**: ^1H NMR (400 MHz, CDCl_3) δ 7.67-7.70 (m, 2H), 7.56-7.59 (m, 2H), 7.33-7.45 (m, 6H), 3.73 (ddd, $J = 11.2, 6.8, 4.0$ Hz, 1H), 2.30 (ddd, $J = 12.4, 7.2, 4.0$ Hz, 1H), 1.87 (octet, $J = 6.8$ Hz, 1H), 1.48-1.74 (m, 3H), 1.37 (dt, $J = 12.4, 11.2$ Hz, 1H), 1.22 (s, 12H), 1.08 (d, $J = 6.8$ Hz, 3H), 0.98 (d, $J = 6.8$ Hz, 3H), 0.77-0.94 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 135.3, 135.1, 134.8, 133.7, 129.9, 129.8, 127.8, 127.6, 83.3, 82.9, 36.7, 34.9, 29.1, 24.8, 24.7, 19.4, 18.3. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (CI) m/z calcd for $\text{C}_{26}\text{H}_{36}\text{BO}_3\text{Si}$ (MH^+): 435.2527, found: 435.2528

10-2. Oxidation of **8**

A mixture of **8** (93 mg, 0.21 mmol), KF (102 mg, 1.8 mmol), KHCO_3 (86 mg, 0.86 mmol), THF (0.2 mL), and MeOH (0.2 mL) was cool to 0°C . H_2O_2 (30% aqueous solution, 0.32 mL) was added slowly to the mixture with stirring. The resulting solution was stirred at room temperature for 12 h. After addition of aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution, the mixture was extracted with AcOEt and the organic layer was dried over anhydrous MgSO_4 . The triol **9** was isolated by column chromatography (AcOEt:MeOH = 30:1). The *anti*- and *syn*-isomers may be separated under these conditions.

(3R*,5S*)-6-Methylheptane-1,3,5-triol (*anti*-9**)**: Oxidation of *trans*-**8** (*trans/cis* = 87:13, 93 mg, 0.21 mmol) was carried out according to the procedure described above. The product *anti*-**9** was isolated in 77% yield (*trans/cis* = 87:13). *anti*-**9**: IR (neat): 3360 cm^{-1} . ^1H NMR (500 MHz, D_2O) δ 3.78-3.83 (m, 1H), 3.57 (t, $J = 6.5$ Hz, 2H), 3.48 (ddd, $J = 10.0, 5.0, 2.5$ Hz, 1H), 1.50-1.61 (m, 3H), 1.45 (ddd, $J = 15.0, 9.5, 2.5$ Hz, 1H), 1.38 (ddd, $J = 15.0, 9.5, 2.5$ Hz, 1H), 0.741 (d, $J = 7.0$ Hz, 3H), 0.735 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz, CD_3OD) δ 74.1, 67.4, 60.6, 42.7, 41.9, 35.7, 19.4, 18.3. HRMS (CI) m/z calcd for $\text{C}_8\text{H}_{19}\text{O}_3$ (MH^+): 163.1334, found: 163.1336.

(3S*,5S*)-6-Methylheptane-1,3,5-triol (*syn*-9**)**: Oxidation of *cis*-**8** (*trans/cis* = 7:93, 75 mg, 0.17 mmol) was carried out according to the procedure described above. The product *syn*-**9** was isolated in 80% yield (*trans/cis* = 7:93). *syn*-**9**: IR (neat): 3360 cm^{-1} . ^1H NMR (400 MHz, D_2O) δ 3.95-4.01 (m, 1H), 3.75 (t, $J = 6.0$ Hz, 2H), 3.63 (ddd, $J = 8.8, 4.8, 4.0$ Hz, 1H), 1.81-1.89 (m, 1H), 1.59-1.78 (m, 4H), 0.94 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (75 MHz, CD_3OD) δ 76.8, 70.1, 60.4, 41.9, 41.0, 35.3, 19.3, 17.9. HRMS (CI) m/z calcd for $\text{C}_8\text{H}_{19}\text{O}_3$ (MH^+): 163.1334, found: 163.1334.

11. ^1H and ^{13}C NMR spectra of the compounds that do not have elemental analysis data

^1H and ^{13}C NMR spectra of **1-3**, *trans*-**4c-f**, *cis*-**4b-f**, *trans*- and *cis*-**8**, and *trans*- and *cis*-**9** are shown in following pages.

STANDARD IN OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Mercury-400BB "varian"
 Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6006.0 Hz
 32 repetitions
 OBSERVE H1, 400.4437670 MHz
 DATA PROCESSING
 FT size 65536
 Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300BB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 15000.0 Hz

400 repetitions

OBSERVE C13, 75.451698 MHz

DECOUPLE H1, 300.067335 MHz

Power 36 dB

Continuously on

WALTZ-16 simulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 56 hr, 44 min, 24 sec

expl std1h

SAMPLE	DATE	Feb	9	2005	dirq	DEC.	& VT
solvent	file	ACQUISITION	exp	dpr	0	0	400.446
at	tn	at	tn	dm	dm	dm	dm
np	sv	42042	6006.0	0	0	0	200
fb	bs	not used	0	0	0	0	0
bs	bs	not used	0	0	0	0	0
tp	tp	58	0	0	0	0	0
pw	pw	6.6	0	0	0	0	0
dl	dl	1.500	0	0	0	0	0
tof	tof	0	0	0	0	0	0
nt	nt	16	0	0	0	0	0
ct	ct	16	0	0	0	0	0
al	al	0	0	0	0	0	0
gain	gain	not used	0	0	0	0	0
FLAGS	FLAGS	0	0	0	0	0	0
il	il	0	0	0	0	0	0
dp	dp	0	0	0	0	0	0
sp	sp	0	0	0	0	0	0
wp	wp	3964	0	0	0	0	0
ac	ac	200	0	0	0	0	0
sc	sc	0	0	0	0	0	0
hw	hw	370	0	0	0	0	0
hram	hram	1.78	0	0	0	0	0
is	is	1486.34	0	0	0	0	0
rf	rf	3869.2	0	0	0	0	0
rfp	rfp	2907.2	0	0	0	0	0
th	th	11	0	0	0	0	0
ins	ins	1.000	0	0	0	0	0
ph	ph	0	0	0	0	0	0

Pulse Sequence: s2pu1

Solvent: CDCl₃Solvent: CDCl₃

Ambient temperature

GEMINI-300BB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec
width 10000.0 v-

630 repetitions

OBSERVE C13, 75.451969

DECOUPLE H1, 300.068733
Power 16 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.0 Hz

FT size 32768

Total time 40 min, 44 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "varian"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6006.0 Hz

32 repetitions

OBSERVE H1 400.4437671 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GBMINI-300NB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

856 repetitions

OBSERVE CH1, 75.4519663 MHz

DECOUPLE H1, 300.0087335 MHz

Power 36 dB

Channel 1 on

WALTZ-16 simulated

DATA PROCESSING

Line broadening 1.0 Hz

PT size 32768

Total time 567 hr, 24 min, 26 sec

3a

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400DB "varian"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6006.0 Hz

24 repetitions

OBSERVE H1, 400.4437673 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

QNP-300WB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

376 repetitions

OBSERVE C13, 75.4519686 MHz

DECOUPLE H1, 300.0687335 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

F1 size 32768

Total time 5674 hr, 4 min, 40 sec

13C OBSERVE

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

QNP-1300MR "varian2"

Relax. delay 1.150 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

600 repetitions

OBSERVE CH1, 75.4519551 MHz

INOCORE F1, 300.0687335 MHz

Power 36 dB

Continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

PT time 32768

Total time 36 min, 56 sec

426

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "varian"

Relax. delay 1.500 sec

Pulse 5.0 degrees

Acq. time 0.100 sec

Width 6006.0 Hz

32 repetitions

OBSERVE F1 400.4438086 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GBMH-300RB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

608 repetitions

OBSERVE C13, 75.4515686 MHz

DECOUPLE H1, 300.0687335 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT 414.37768

Total time 36 min, 56 sec

134.793

129.460

128.338

128.153

127.707

127.677

125.448

135.101

142.724

136.991

136.945

116.779

83.794

77.415

77.000

76.570

73.449

41.678

38.235

31.749

25.078

STANDARD 1H OBSERVE

Pulse Sequence: a2pul

Solvent: CDCl3

Ambient temperature

Mercury-400NB "varian"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6006.0 Hz

32 repetitions

OBSERVE H1, 400.4437677 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

QNP-100WB "varian"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

1024 repetitions

OBSERVE C13, 75.4519698 MHz

INCOUPLE H1, 300.0687335 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 39 min, 13 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400NB "varian"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6006.0 Hz

24 repetitions

OBSERVE H1, 400.4437673 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GBMINI-300HB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

320 repetitions

OBSERVE CH3, 75.451975 MHz

DECOUPLE H1, 300.0687335 MHz

Power 36 dB

Continuously on

WALTZ-16 modulated

DDN, ROCKING

Line Broadening 1.0 Hz

PT 418.37768

Total time 5674 hr, 4 min, 40 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz

32 repetitions

OBSERVE H1 400.4437670 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GBMNI-300HS "varian2"

Relax. Delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

808 repetitions

OBSERVE C13, 75.4515663 MHz

DECOUPLE H1, 300.0687335 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

160 Processing 1.0 Hz

FT 81.32768 Hz

Total time 56 hr, 44 min, 24

STANDARD 1F OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400NB "varian"

Relax delay 1.500 sec

Pulse 45.0 degrees

Acq time 3.500 sec

Width 6006.0 Hz

32 transients

OBSERVE H1 400.4437677 MHz

DATA PROCESSING

PT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

QNP1H-300MH "varian2"

Relax. delay 1.156 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

200h repetitions

200h scans

OBSERVE CH1, 75.451675 MHz

PROBHD1 CH1, 300.068735 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 567 hr, 24 min, 26 sec

127.569
129.675
129.721
133.456
134.655
135.224

135.546

75.540
76.585

77.430
77.000

82.995

46.889

41.356

24.971
24.525

25.124

22.234
22.511

17.900

12.244

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "varian"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6006.0 Hz

32 repetitions

OBSERVE H1, 400.4437671 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

```
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"
```

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
8944 repetitions

OBSERVE C13, 75.4519651 MHz
 DECOUPLE H1, 300.0687335 MHz
 Power 36 dB
 continuously on
 WALZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 32768
 Total time 567 hr, 24 min, 26

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400DB "varian"

Relax delay 1.500 sec

Pulse 45.0 degrees

Acq time 3.500 sec

Width 6005.0 Hz

32 repetitions

OBSERVE H1 400.4437675 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

QNP1H-300MHz "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

1704 repetitions

OBSERVE C13, 75.4519663 MHz

DECOUPLE H1, 300.0687335 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 567 hr, 24 min, 26 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "varian"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6006.0 Hz

28 repetitions

OBSERVE H1, 400.4437671 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300HB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

808 repetitions

OBSERVE C13, 75.4515675 MHz

DECOUPLE H1, 300.0687335 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT date 3/27/88

Total time 567 hr, 24 min, 26 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Mercury-400BB "varian

Relax. delay 1.500 se

Pulse 45.0 degrees
Acq. time 3.500 sec

Width 6006.0 Hz

32 repetitions

OBSERVE H1, 400.4437

DATA PROCESSING
FT size 65536

Total time 3 min, 2 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "varian"

Relax delay 1.500 sec

Pulse 45.0 degrees

Acq time 3.500 sec

Width 6006.0 Hz

32 repetitions

OBSERVE H1 400.4437673 MHz

DATA PROCESSING

FT size 65536

Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300HB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

312 repetitions

OBSERVE CH, 75.4519663 MHz

DECOUPLE H1, 300.0697335 MHz

Power 36 dB

Continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT 418.37268

Total time 56740 hr, 46 min, 56 sec

STANDARD 1H OBSERVE

```
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.443767
DATA PROCESSING
FFT size 65536
Total time 3 min, 2 sec
```

```
Pulse Sequence: s2pul
Solvent: CDC13
Ambient temperature
GEMINI-300BB "varian2
```

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
1032 repetitions
OBSERVE C13, 75.4519686 MHz
DECEPTE H1, 300.0687335 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
F2 size 32768
Total time 5674 hr, 4 min, 40

33963
35423

12.10 12.10

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

QNP1H-300MB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

720 repetitions

OBSERVE C13, 75.4515663 MHz

DECOUPLE H1, 300.0687335 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 567 hr, 24 min, 26 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400HB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
32 repetitions

OBSERVE HL, 400.4437682 MHz
DATA PROCESSING
F1 size 65536
Total time 3 min, 2 sec

13C OBSERVE

Pulse Sequence: zgpg30
Solvent: CDCl3
Ambient temperature
GEMINI-300SB "vaxim2"

Relax. delay 1.150 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 18000 Hz
1360 repetitions
OBSERVE C13, 75.4515583
DECOUPLE H1, 300.0061331
Power 36 dB
Modulated continuously on

WDW-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768

Total time 56740 hr, 45 min

ALPHA COMMONY_DEFAULT.ALS
101-anti

DEFILE C:\X\N\ALPHA\COMMONY_DEFAULT
CONVI triol-anti
DATUM Wed Jul 26 12:36:10 200
ORNUC 1H
EXMCD SINGL 500.00 MHz
ORFRO 162410.00 Hz
ORFTN 32768
POINT 10000.00 Hz
FREQU 16
SCANS 3.2768 sec
ACQTM 2.2232 sec
PD 6.75 usec
PMT 1H
TRNUC 24.2 c
CTEMP 4.63 ppm
SLVNT D2O
EXREF 0.49 Hz
RGAIN 15

13C OBSERVE

Pulse Sequence: zgpg30

Solvent: CD3OD

Acq. time 0.842 sec

Width 19000.0 Hz

496 repetitions

OSERVE C13, 75.4321350 MHz

MEASURE H1, 300.0639138 MHz

Power 36 dB

continuously on

NAUT-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 39 min, 13 sec